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Subj: Hydrogen evolution rates for mine batteries and selection of a hydrogen getter; information on

Ref: (a) Fleischer, A. and Lander, J.J. Zinc - Silver Oxide Batteries. New York: John Wiley and Sons, Inc., 1971.
(b) Hampez, C. The Encyclopedia of Electrochemistry. New York: Reinhold Publishing Corporation, 1964.
(c) Reduction of Hydrogen in Mines. Report of American Ordnance Association, Nov. 1, 1964.

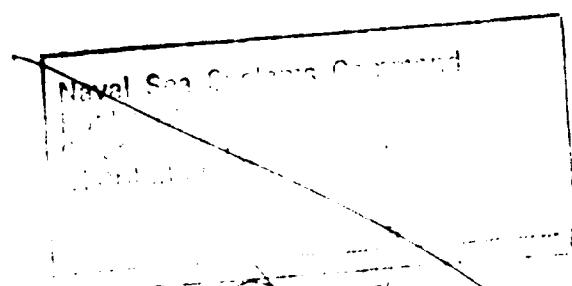
I. ABSTRACT

Mine batteries evolve hydrogen at various rates. In one month at 32°C, volumes ranged from roughly 33 milliliters for Battery Mk 114 Mod 0 to 3 milliliters for Battery Mk 121 Mod 0. At 32°C, F, F50, and F96 cells used in Leclanche batteries produced roughly 0.5 to 2 milliliters of hydrogen per cell in one month. Cells of the 3-AH and R-4R types, used in cadmium-mercuric oxide and zinc-mercuric oxide batteries respectively, produced about 0.4 to 0.6 milliliters of hydrogen. Palladium and palladium oxide getters were selected to eliminate free hydrogen in sealed environments containing mine batteries.

II. INTRODUCTION

In the early 1970's the Naval Mine Engineering Facility investigated various aspects of hydrogen evolution by mine batteries. This report summarizes data collected on hydrogen evolution rates for specific mine batteries and discusses the selection of a hydrogen getter.

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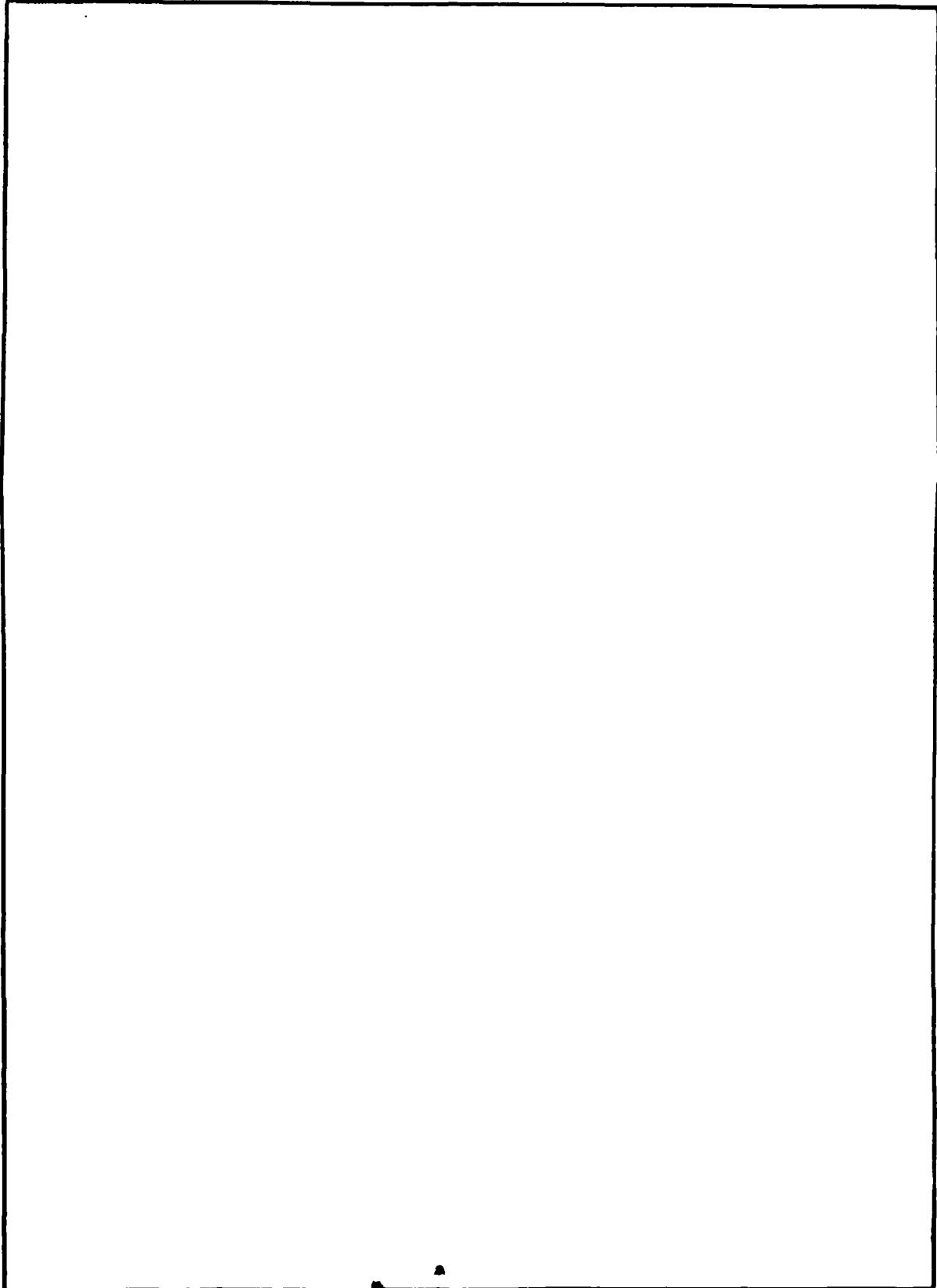


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Mine batteries evolve hydrogen at various rates. In one month at 320C, volumes ranged from roughly 33 milliliters for Battery Mk 114 Mod 0 to 3 milliliters for Battery Mk 121 Mod 0. At 320C, F, F50, and F96 cells used in Leclanche batteries produced roughly 0.5 to 2 milliliters of hydrogen per cell in one month. Cells of the 3-AH and R-4R types, used in cadmium-mercuric oxide and zinc-mercuric oxide batteries respectively, produced about 0.4 to 0.6 milliliters of hydrogen. Palladium and palladium oxide getters were selected to eliminate free hydrogen in sealed environments containing mine batteries.		

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III. HYDROGEN EVOLUTION RATES FOR SPECIFIC MINE BATTERIES

A. Experimental Procedures

1. Containers Mk 23, which are rugged aluminum containers designed to hold gases, were instrumented with valves and polyethylene tubing. Tubing was placed in each container, which has a volume of about 5750 milliliters, to allow for external sampling of the internal environment at three places: top, middle, and bottom. Figure 1 illustrates the external appearance of one container.

2. Samples of the mine batteries identified below were randomly selected from available stocks. Conformance of the batteries to all specified requirements for fresh batteries was verified by applicable tests.

Battery	Cell Chemistry	Cell Designation per ANSI*	Number of Cells
Mk 109 Mod 0	Leclanche	F (cylindrical)	6
Mk 110 Mod 0	Leclanche	F (cylindrical)	4
Mk 111 Mod 0	Leclanche	F (cylindrical)	4
Mk 112 Mod 0	Leclanche	F (cylindrical)	8
Mk 113 Mod 0	Leclanche	F96 (flat)**	15
Mk 114 Mod 0	Leclanche	F50 (flat)**	60
Mk 115 Mod 0	Leclanche	F (cylindrical)	2
Mk 117 Mod 0	Cadmium-Mercuric Oxide	3-AH	18
Mk 119 Mod 1	Zinc-Mercuric Oxide	R-4R	12
Mk 121 Mod 0	Cadmium-Mercuric Oxide	3-AH	5

3. Two to three of each type of mine battery were placed in an instrumented Container Mk 23. Batteries were in the as-received, no-load condition. Each container was sealed and placed in a controlled environment at 21°C (70°F) or 32°C (90°F).

4. The concentration of hydrogen in each container was determined at periodic time intervals using an Explosimeter Model 3 made by Mine Safety Appliance Company and calibrated with standard air/hydrogen mixtures. Concentrations of hydrogen were recorded as a percentage of the lower explosive limit (L.E.L.), which is 4% hydrogen in 96% air.

B. Results

Average concentrations of evolved hydrogen versus time for the mine batteries identified in paragraph III.A.2 are given in Figures 2 through 11.

*ANSI - American National Standards Institute

**Specifications state that Battery Mk 113 Mod 0 usually contains A cells and that Battery Mk 114 Mod 0 usually contains N cells. However, for the tested batteries flat cells very similar to ANSI F96 and F50 were used as noted.

C. Discussion of Results

1. Data collected for individual mine batteries showed that batteries can be ranked in the following order of decreasing hydrogen production:

Battery	Cell Designation and Number of Cells	Estimated Volume of Hydrogen Evolved In One Month at 32°C (Milliliters)
Mk 114 Mod 0	F50, 60	33
Mk 113 Mod 0	F96, 15	25
Mk 112 Mod 0	F, 8	9
Mk 109 Mod 0	F, 6	8
Mk 111 Mod 0	F, 4	7
Mk 110 Mod 0	F, 4	7
Mk 117 Mod 0	3-AH, 18	6
Mk 119 Mod 1	R-4R, 12	5
Mk 115 Mod 0	F, 2	4
Mk 121 Mod 0	3-AH, 5	3

2. Based on data presented in Figures 2-11 for individual batteries in the no-load condition, it was estimated that F, F50 and F96 cells used in Leclanche batteries produced roughly 0.5 to 2 milliliters of hydrogen in one month at 32°C (90°F). Cells of the 3-AH and R-4R types, used in cadmium-mercuric oxide and zinc-mercuric oxide batteries respectively, produced about 0.4 to 0.6 milliliters of hydrogen in one month at 32°C (90°F). At 21°C (70°F), F, F50 and F96 cells produced about 0.1 - 0.3 milliliters whereas 3-AH and R-4R cells produced 0.1 - 0.3 milliliters. These data generally support the observation that the rate of most chemical reactions is roughly doubled or tripled by a 10°C rise in temperature. Based on data collected at 21°C and 32°C, rates of hydrogen evolution at higher or lower storage temperatures for the as-received batteries can be approximated. No data were collected for batteries under discharge. However, evolution rates for hydrogen are expected to be greater for batteries under discharge than for batteries under the no-load, stowage mode.

IV. SELECTION OF A HYDROGEN GETTER

A. Potential Getters

1. Hydrogen burner

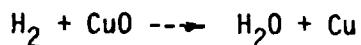
The hydrogen burner, which has been used in certain torpedoes as a hydrogen getter, consists of an electrically heated filament that serves as an ignition source for mixtures of oxygen and hydrogen. In operation the burner is very similar to the operation of the Explosimeter Model 3 used to determine concentrations of hydrogen evolved from mine batteries. In a closed environment where hydrogen is produced slowly by batteries, the reaction rate on the burner is essentially imperceptible. Thus, the burner represents a relatively safe and effective getter. The burner does, however, have two major disadvantages. If the oxygen supply in the closed environment is depleted and excess hydrogen collects, opening of the container is hazardous

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since the hot burner might ignite the resulting hydrogen/oxygen mixture. In addition, the burner requires auxillary electrical equipment, which might be difficult to fit into the closed environment.

2. Fuel cell

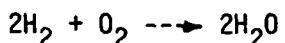
Small fuel cells for combining hydrogen and oxygen on board Explorer satellites were developed by the General Electric Corporation and the National Aeronautics and Space Administration. Most of those cells used hydrogen as the anode, copper oxide as the cathode and an alkaline electrolyte for an overall cell reaction of:



As discussed in reference (a), the cells conveniently and effectively solved the hydrogen problem for the spacecraft. However, the cells were made especially for use on Explorers and were never produced in large quantities. As far as the Facility was able to determine, such small fuel cells are not readily available from General Electric or from other manufacturers. Thus, procurement of fuel cells for use in sealed containers with batteries would be an involved and costly process.

3. Palladium metal

a. Palladium metal is probably the most efficient of all known hydrogen getters. Reference (b) estimates that 900 volumes of hydrogen can be absorbed by one volume of palladium to form an interstitial solid solution. In addition to this reaction, palladium also serves as a catalytic surface for the reaction:



Palladium metal on an alumina substrate was used in the past as a hydrogen getter in certain weapons containing lead-acid batteries, which frequently produce large volumes of hydrogen.

b. One potential disadvantage of all palladium metal getters involves the modes of reaction. As discussed in reference (c), if a container with batteries and a palladium getter remain sealed for a very long period of time, the oxygen supply inside the container might be depleted because of the reaction between hydrogen and oxygen. In addition, if the time were sufficiently long, the getter might absorb its total capacity of hydrogen. If both of these events occurred, excess hydrogen could collect in the sealed container. When the container is opened, in-rushing air might lead to a rapid reaction of hydrogen and oxygen on the surface of the getter. Consequently, the getter might generate enough heat to serve as an ignition source for the remaining hydrogen/air mixture. Another disadvantage is the formation of free water during the reaction of hydrogen and oxygen. This water can possibly serve as a corrosive agent for enclosed equipment.

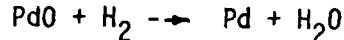
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4. Palladium black

Palladium black is palladium metal in a powdered form. It reacts with hydrogen in the same manner as unpowdered palladium and possesses essentially the same advantages and disadvantages.

5. Palladium oxide

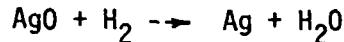
Palladium oxide reacts with hydrogen according to the following reaction:



Palladium produced from the reaction is then available as a secondary getter to absorb hydrogen and to serve as a catalytic surface for the reaction of hydrogen and oxygen. From a theoretical standpoint, palladium oxide has some advantage over palladium metal as a getter. Since the oxide carries an internal oxygen supply, a longer time can elapse in a closed environment before the getter itself becomes potentially hazardous. In addition, palladium oxide is a proven getter. As discussed in reference (a), it was used on board some Explorer satellites.

6. Silver oxide

Divalent silver oxide reacts with hydrogen according to the following reaction:



As discussed in reference (c), this getter was recommended by the American Ordnance Association for use in mines primarily because it does not heat up appreciably during rapid reaction of hydrogen/air mixtures. Thus, opening a hydrogen-containing weapon with a silver oxide catalyst is potentially less hazardous than opening one with a palladium catalyst. Offsetting this advantage are two disadvantages. First, the divalent form of silver oxide is apparently difficult to purchase. A check of catalogs for six major chemical supply companies showed that none offered divalent silver oxide for sale. Second, the oxide decomposes thermally to produce silver and oxygen. Thus, the shelf life of the getter would be limited.

7. Proprietary getter of Union Carbide

Since hydrogen evolution is a consequence of battery design and fabrication, leading battery manufacturers were contacted to determine if proprietary getters are available. Union Carbide Corporation responded by designing a getter consisting of a bag of grey material that reacts directly with hydrogen to produce a compound with no free water. Tests



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showed that this getter effectively eliminated free hydrogen. The getter was more costly than palladium-on-alumina getters but less costly than the other getters. Production estimates showed that required quantities of this getter would be available within a slightly longer time frame than palladium-on-alumina and palladium oxide getters.

B. Ranking of potential getters

For use in enclosed areas containing the batteries identified in Paragraph III.A.2, the potential getters were ranked in the following order of decreasing acceptability:

1. Palladium on alumina
2. Proprietary getter of Union Carbide
3. Palladium oxide
4. Palladium black
5. Silver oxide
6. Fuel cells
7. Hydrogen burner

C. Evaluation of getters

Three configurations of palladium-on-alumina getters, the proprietary getter of Union Carbide, and one configuration of a palladium oxide getter were tested extensively in hydrogen-air environments. All getters effectively eliminated free hydrogen in enclosed containers. Generation of heat on the surfaces of palladium getters during rapid reactions of hydrogen and oxygen was shown not to be a problem. For getters producing free water, tests showed that addition of desiccants to the containers solved this problem effectively. Because of cost and ready availability, the palladium-on-alumina configurations were selected for use in the mine program.

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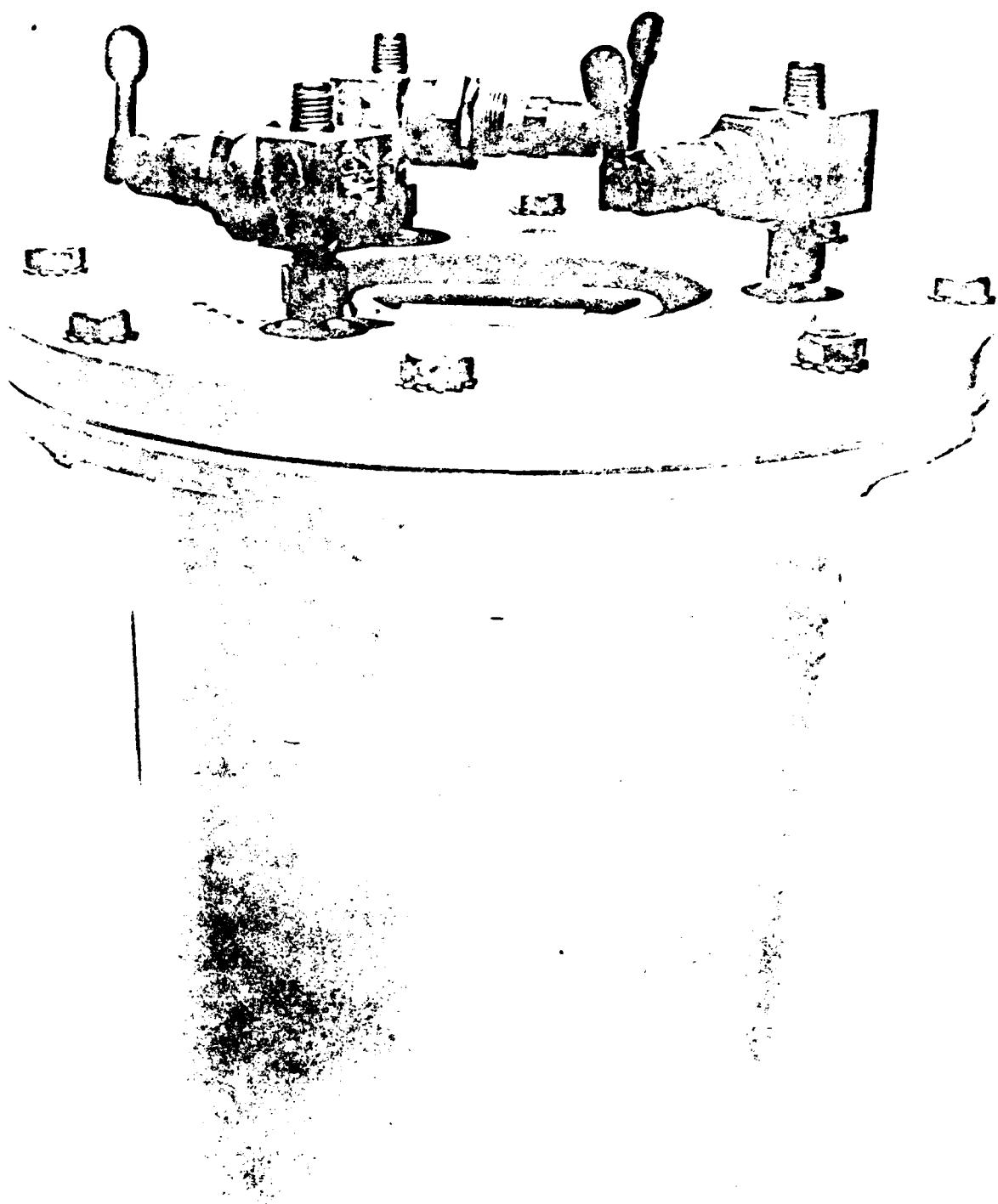


FIGURE 1. INSTRUMENTED CONTAINER MK 25

FIGURE 2

EVOLUTION OF HYDROGEN BY THREE BATTERIES MK 109 MOD 0 IN CONTAINER MK 23

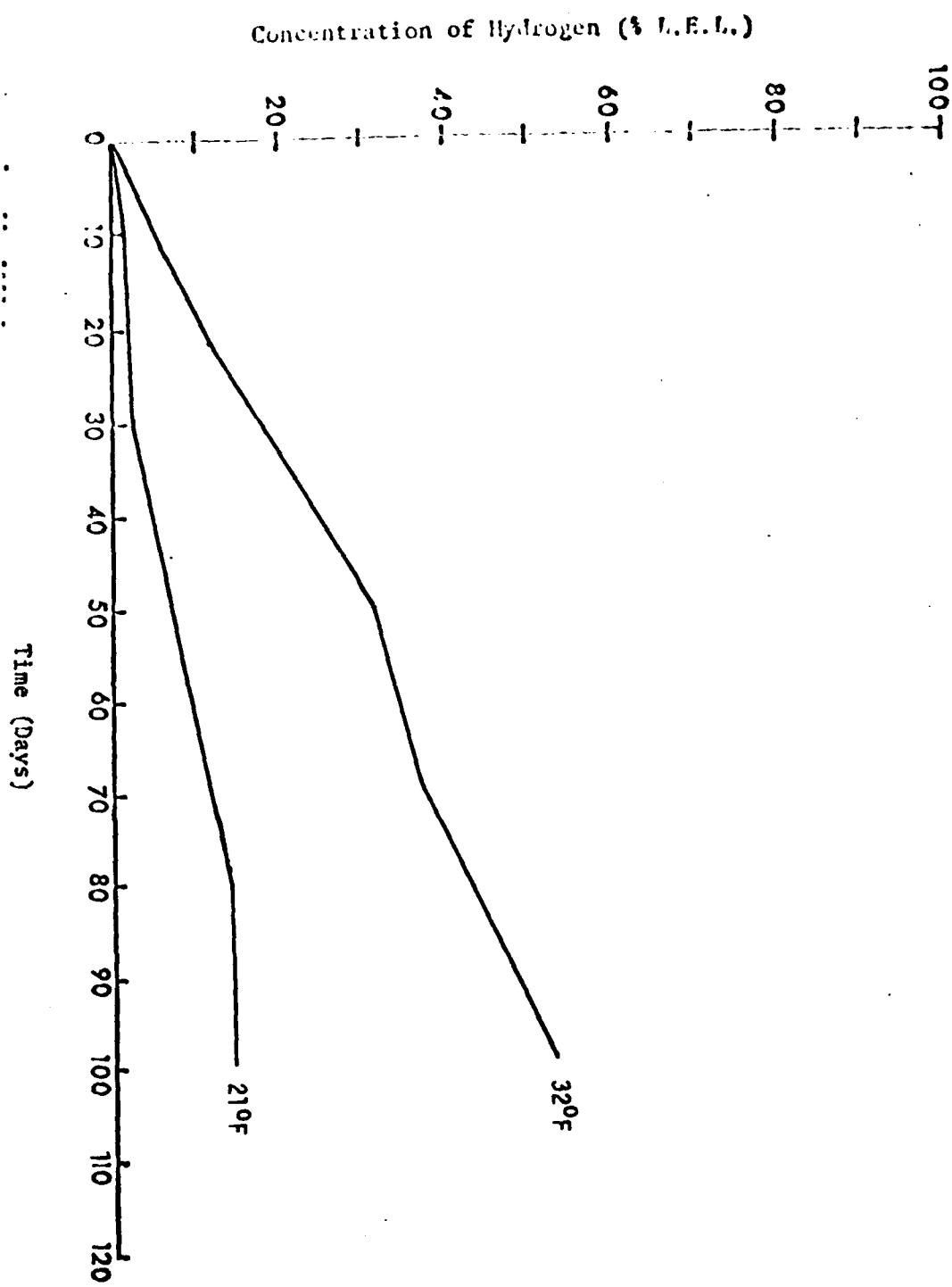


FIGURE 3

EVOLUTION OF HYDROGEN BY TWO BATTERIES MK 110 MOD 0 IN CONTAINER MK 23

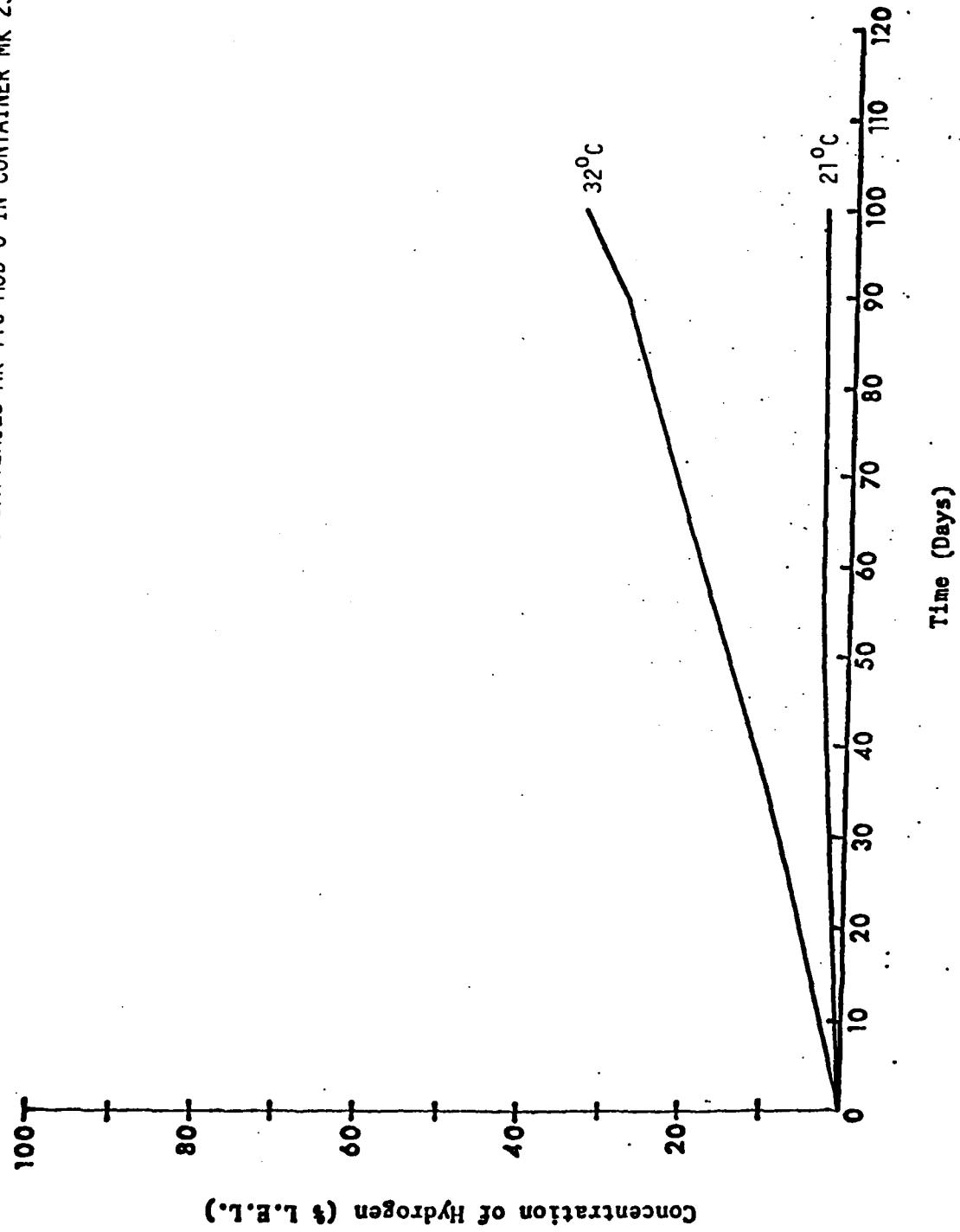


FIGURE 4

EVOLUTION OF HYDROGEN BY THREE BATTERIES MK 111 MOD 0 IN CONTAINER MK 23

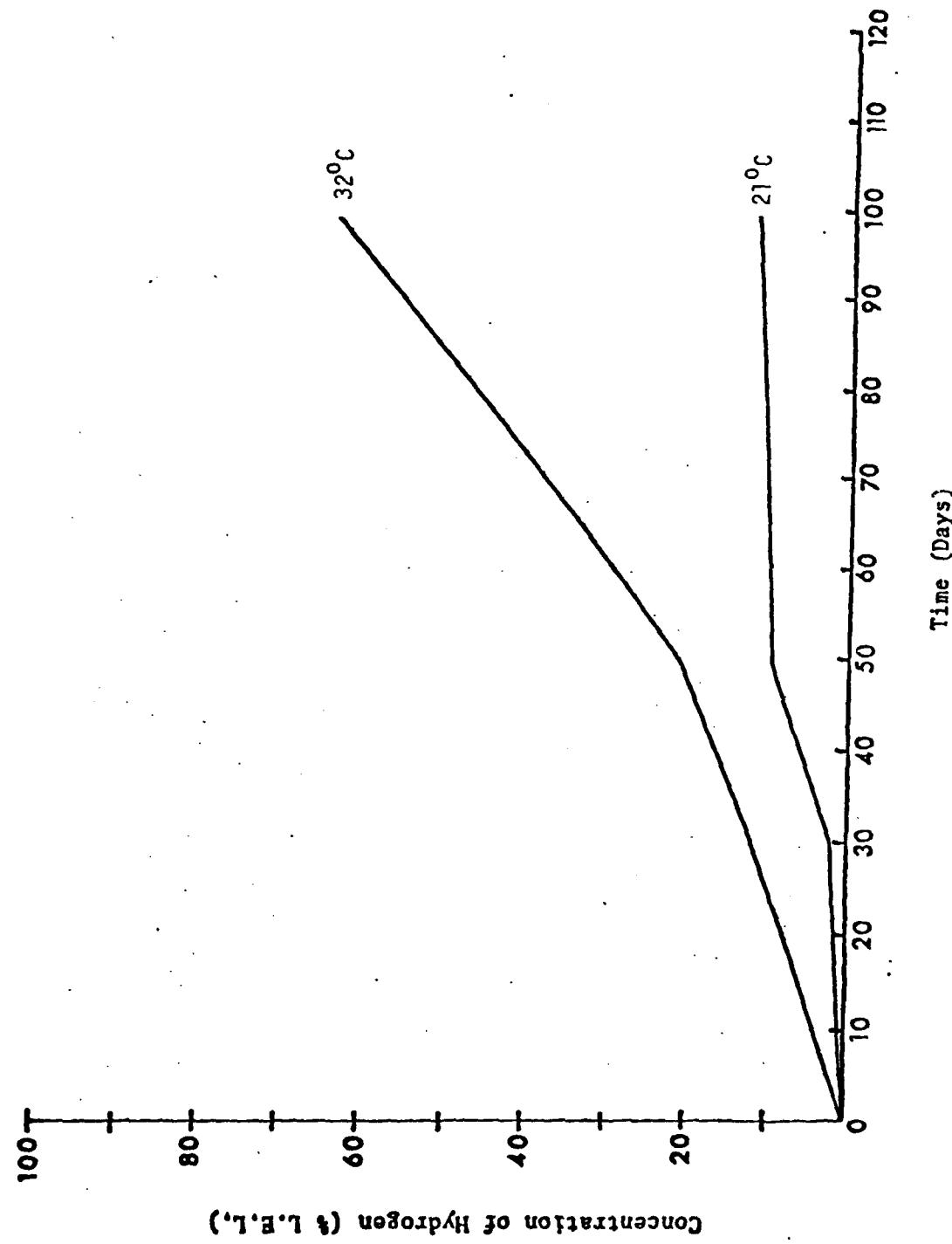


FIGURE 5

EVOLUTION OF HYDROGEN BY THREE BATTERIES MK 112 MOD 0 IN CONTAINER MK 23

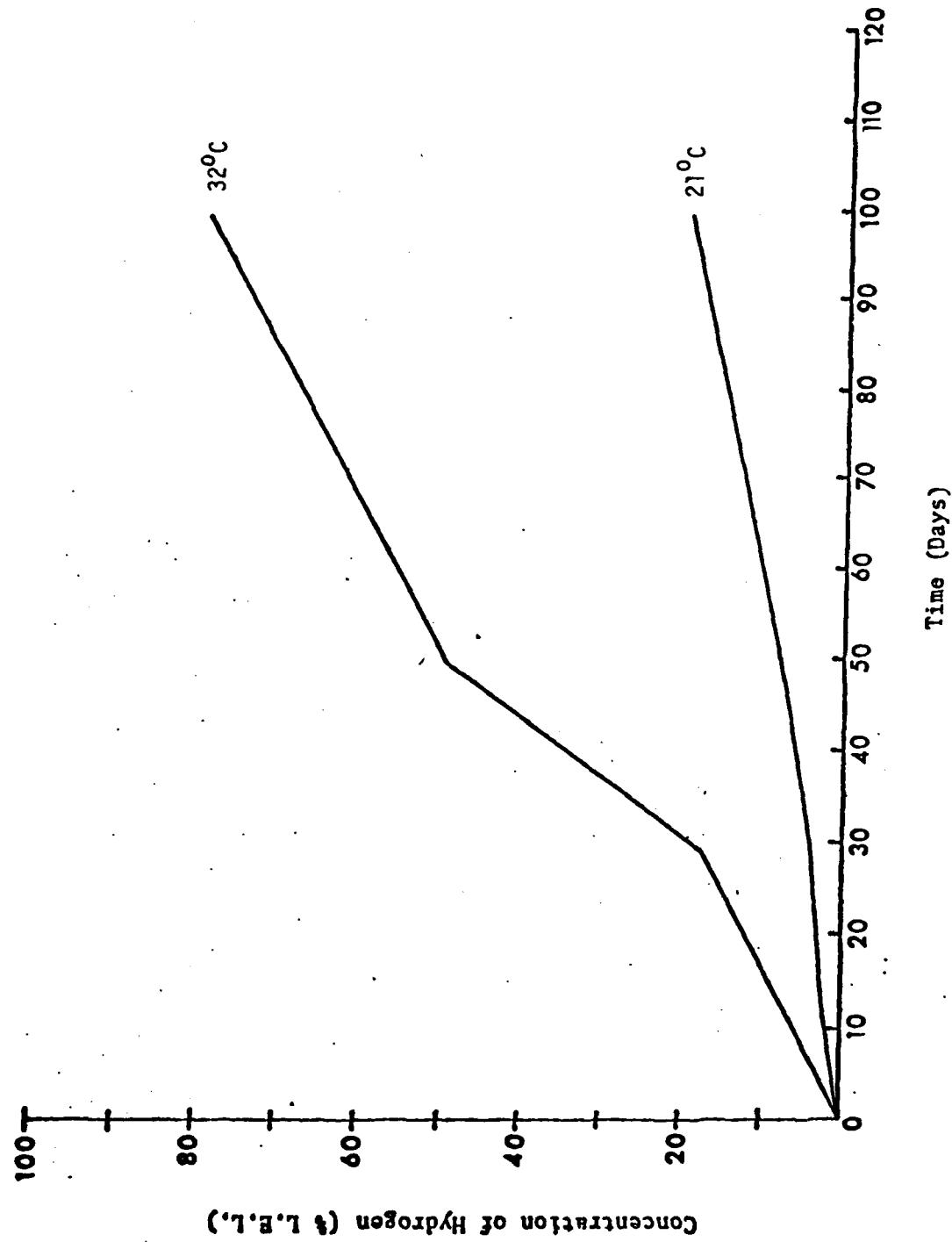


FIGURE 6

EVOLUTION OF HYDROGEN BY TWO BATTERIES MK 113 MOD 0 IN CONTAINER MK 23

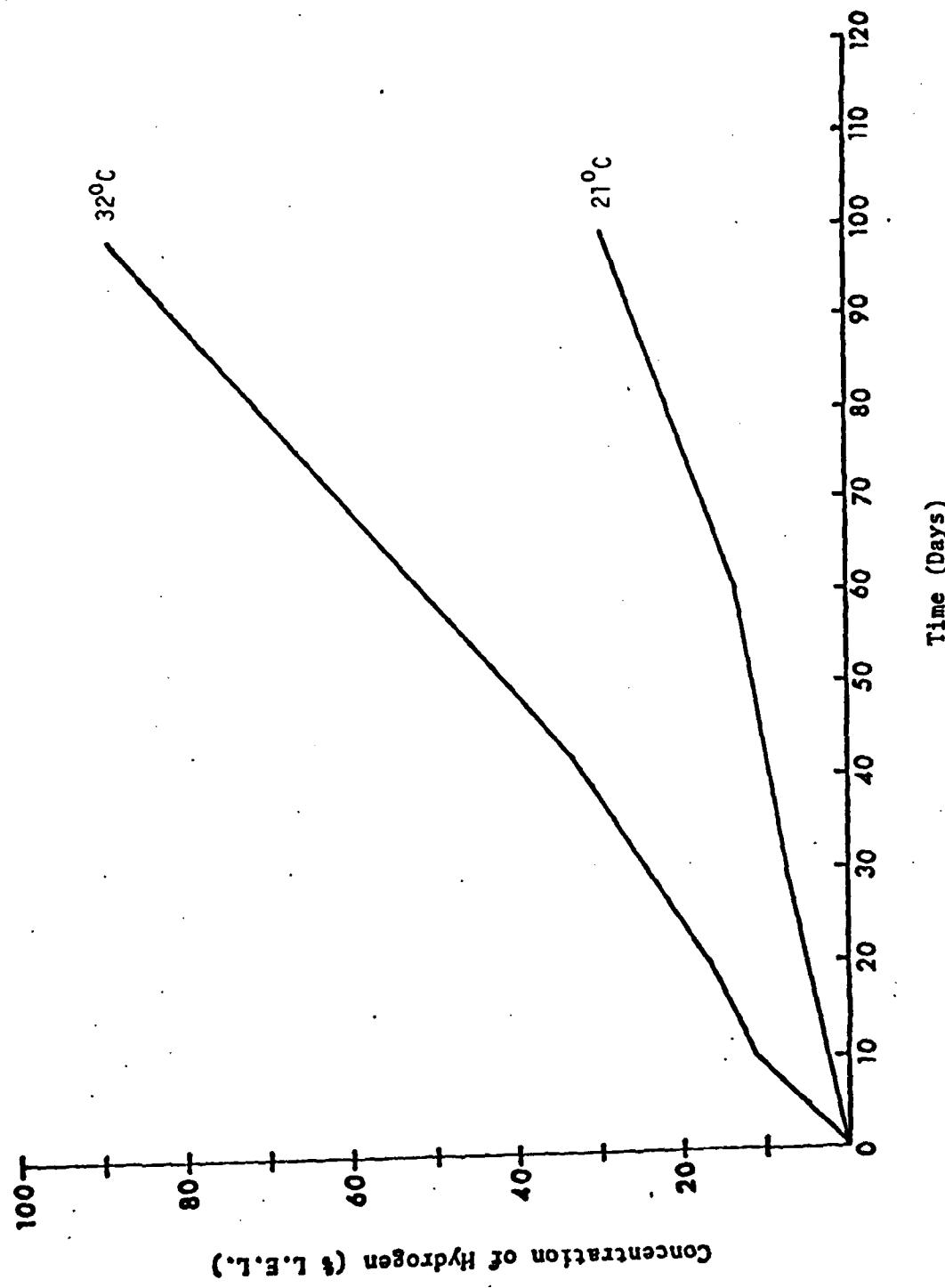


FIGURE 7
EVOLUTION OF HYDROGEN BY TWO BATTERIES MK 114 MOD 0 IN CONTAINER MK 23

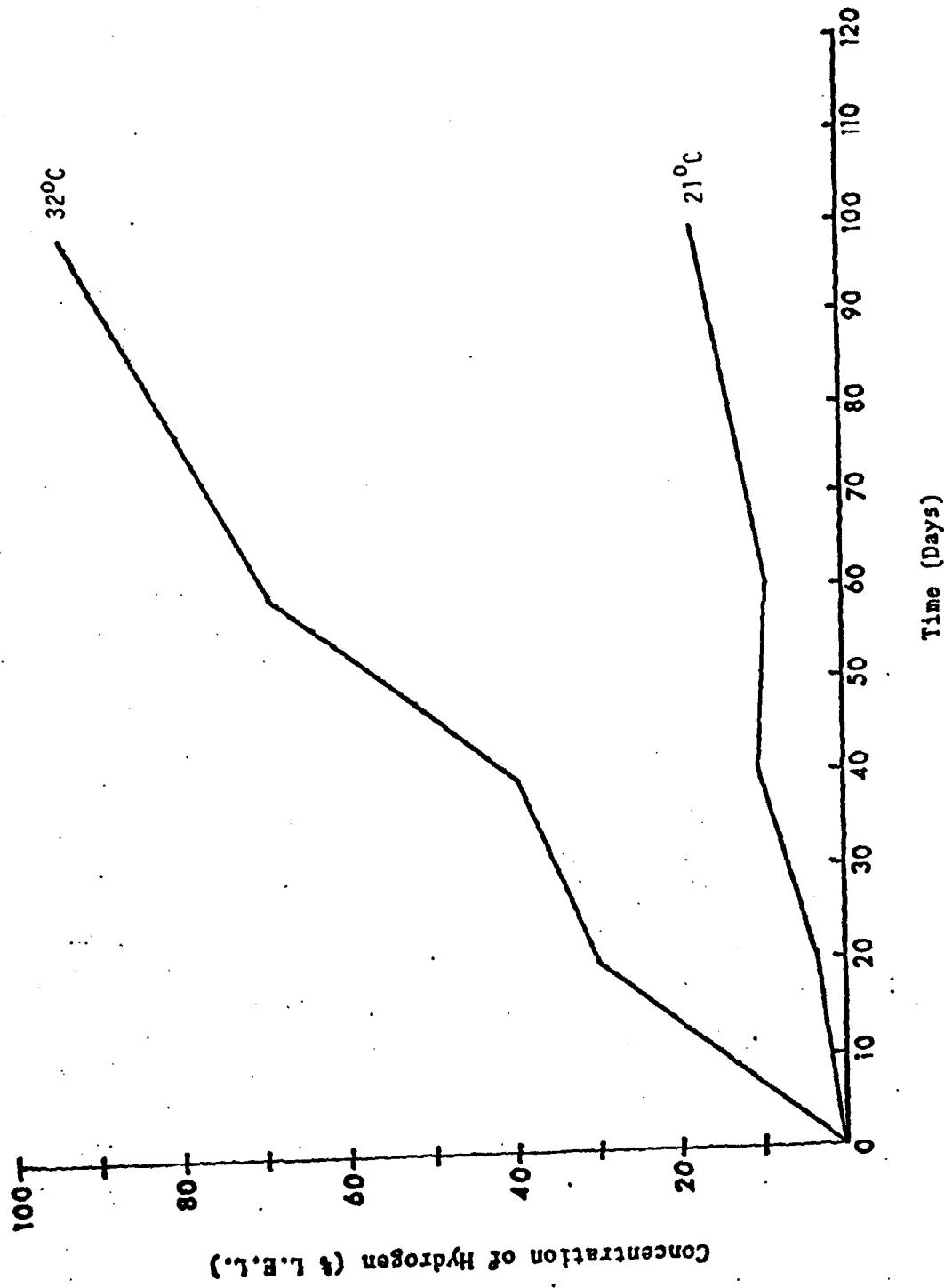


FIGURE 8

EVOLUTION OF HYDROGEN BY TWO BATTERIES MK 115 MOD 0 IN CONTAINER MK 23

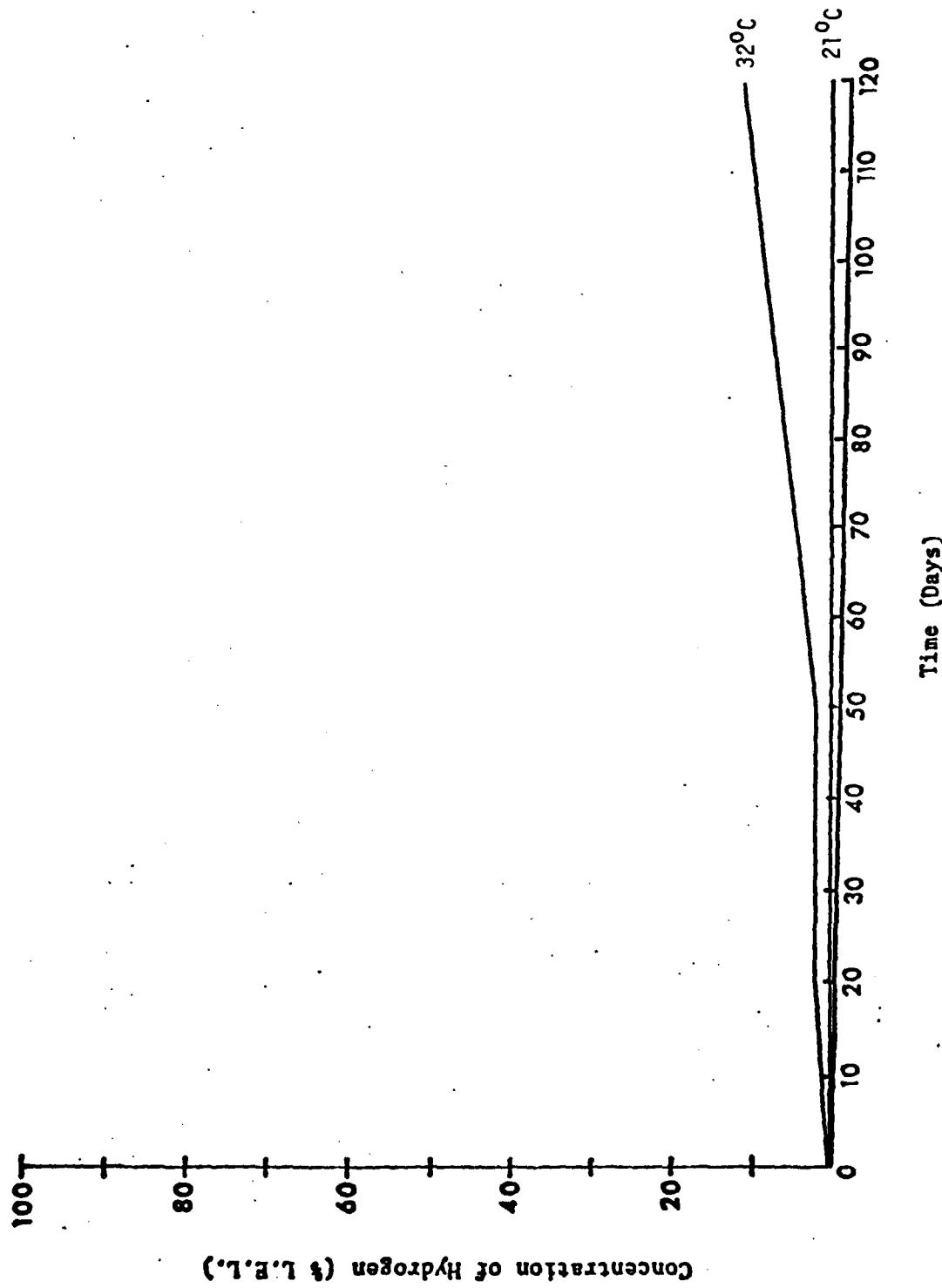


FIGURE 9

EVOLUTION OF HYDROGEN BY THREE BATTERIES MK 117 MOD 0 IN CONTAINER MK 23

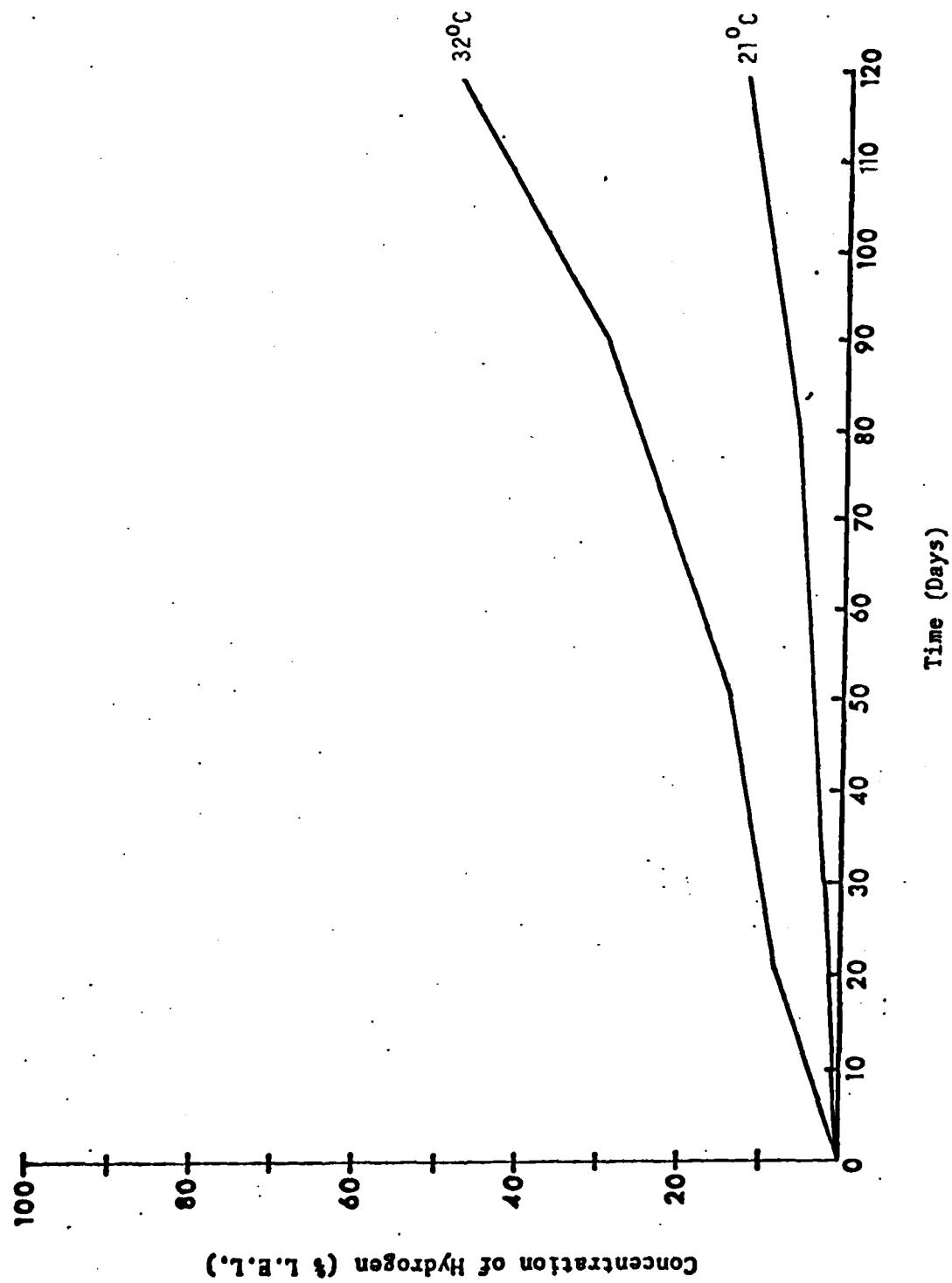


FIGURE 10

EVOLUTION OF HYDROGEN BY THREE BATTERIES MK 119 MOD 1 IN CONTAINER MK 23

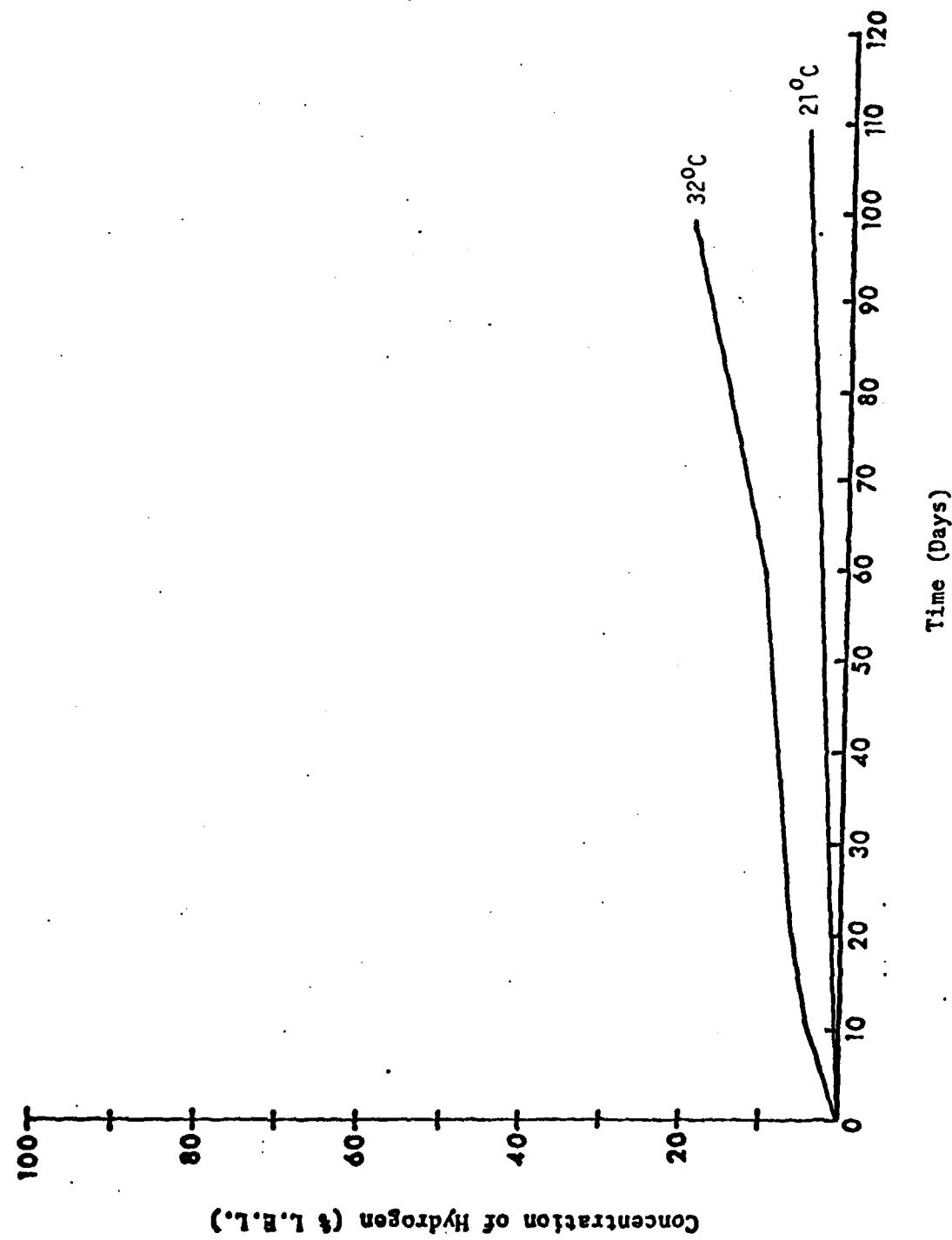


FIGURE 11
EVOLUTION OF HYDROGEN BY TWO BATTERIES MK 121 MOD 0 IN CONTAINER MK 23

